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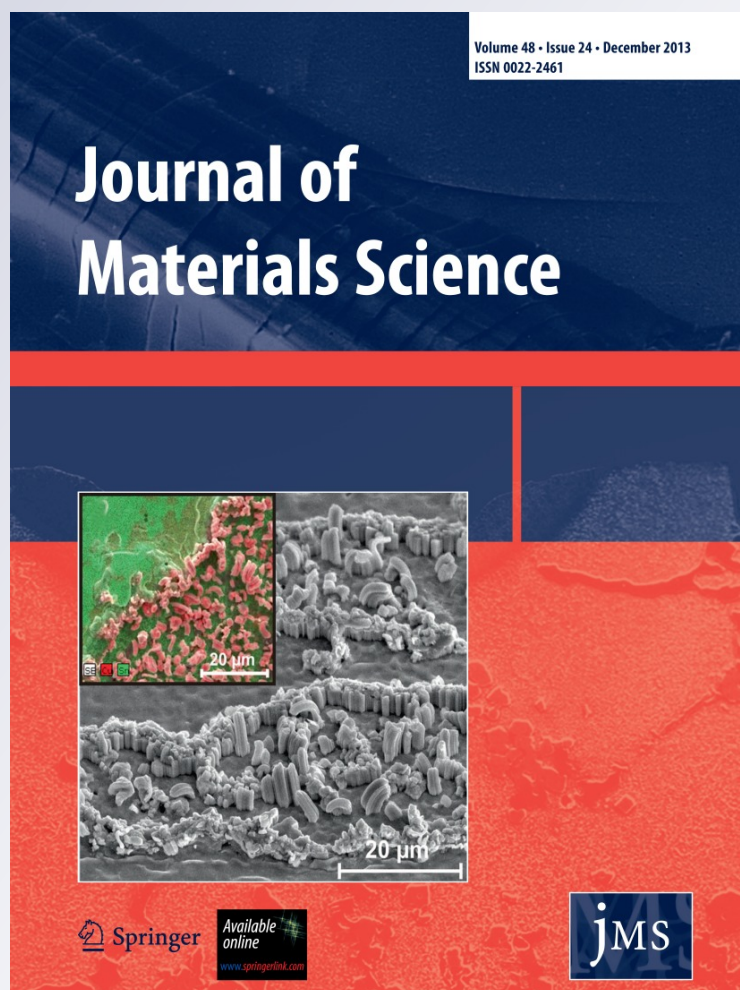
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# Dispersion of gold dodecanethiolate in a silsesquioxane film with pendant dodecyl chains: from photoluminescent materials to gold nanocomposites

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**Abstract** Photoluminescence of Au(I)-dodecane thiolate (Au(I)-DDT) and its thermal reduction to metallic gold have been extensively reported in the literature. However, the incorporation of this salt to a polymeric matrix to produce photoluminescent materials or gold nanocomposites by thermal reduction is a difficult task due to the insolubility of Au(I)-DDT. In this study it is shown that a silsesquioxane with pendant dodecyl chains can be a convenient host of Au(I)-DDT. The presence of dodecyl chains in both compounds and the in situ generation of the salt in the solution of the silsesquioxane precursor enabled to obtain a uniform dispersion of Au(I)-DDT in the silsesquioxane matrix. Flexible films were generated, exhibiting characteristic photoluminescent properties before thermal treatment and a uniform dispersion of gold nanoparticles after heating at 150 °C for different periods of time.

## Introduction

Noble metal nanoparticles (NP) are of considerable interest in a wide range of applications ranging from catalysts and medical diagnostic tests to sensors and optoelectronic

devices such as optical keys, ultrafast filters, and polymeric light emitting diodes. In particular, nanocomposites based on a dispersion of NP in a polymer have attracted great interest in several of these applications [1–3]. Polymer nanocomposites can be prepared by in situ synthesis of NP in polymer matrices with or without reducing agents [4–8], or by blending preformed NP and polymers [9–11]. A fundamental step toward the development of specific applications is the control of the size and shape of NP and their spatial array in the final device [12, 13].

Gold NP are particularly interesting due to their non-toxicity [14], biocompatibility, photochemical properties [15], ease of imaging, and versatility of the surface chemistry [16, 17]. Usual precursors for obtaining Au NP are Au(I) alkane thiolates. These compounds have luminescent properties and are capable of acting as precursors for the production of Au NP by thermal reduction [18, 19]. However, due to the very low solubility of Au(I) alkane thiolates in most solvents it is difficult to generate uniform dispersions of Au NP in a polymer employing this technique [20].

Bridged silsesquioxanes are a family of organic–inorganic hybrid materials synthesized by the hydrolysis and condensation of monomers containing an organic bridging group joining two (or eventually more) trialkoxysilane groups. Bridged silsesquioxanes were previously used for the dispersion of dyes [21, 22], hierarchical assemblies of Au NP [23], and silver thiolate complexes [24].

The aim of this study is to show that a bridged silsesquioxane with pendant dodecyl chains is a convenient host to disperse Au(I) dodecanethiolate (Au(I)-DDT) and to generate a uniform dispersion of Au NP by thermal reduction. Flexible films with photoluminescent properties were generated that were converted into gold nanocomposites by thermal reduction.

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## Materials and methods

### Materials

Dodecylamine (DA, Fluka, 98 % purity) and glycidoxypropyltrimethoxysilane (GPTMS, Sigma, 97 % purity) were used without further purification. Dodecanethiol (DDT), hydrogen tetrachloroaurate (III) trihydrate (Aldrich,  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ,  $\geq 49$  wt% as Au), and formic acid (Sintorgan) were used as-received. Tetrahydrofuran (THF, Cicarelli) was refluxed in KOH and distilled over 4 Å molecular sieves. Water was purified through a Millipore Milli-Q system. The synthesis of the materials will be discussed in detail in the “Results and discussion” section.

### Characterization techniques

X-ray diffraction spectra of films were obtained in the  $2\theta$  range comprised between  $2^\circ$  and  $60^\circ$ , using an X'Pert Pro PANalytical diffractometer equipped with a graphite monochromator, proportional detector, and a  $\text{Cu K}\alpha$  radiation source.

Differential scanning calorimetry (DSC) thermograms were obtained with a DSC-50 Shimadzu equipment at a heating rate of  $10^\circ\text{C}/\text{min}$ , under  $\text{N}_2$  flow.

Scanning electron microscopy images were obtained with different devices: JEOL JSM-6460LV SEM provided with an EDAX analyzer (Genesis Spectrum V5.11), Zeiss DSM 982 Gemini FEG-SEM Microscope, and FESEM Zeiss Supra 40.

Surface hydrophobicity was evaluated by using the initial static contact angle technique. Photographs were taken with a digital camera after stabilization of the drop deposited on the film surface (about 5 min). Reported results correspond to the average values of eight independent measurements.

Absorption spectra of films (500  $\mu\text{m}$  thickness) were obtained using a conventional diode-array UV–Vis spectrophotometer (Hewlett-Packard 8453) with a holder adapted for solid samples. Steady state emission spectra of the films were obtained at  $(20 \pm 2^\circ\text{C})$  using a Spex Fluoromax spectrofluorometer. A solid sample holder placed at  $45^\circ$  was employed to record the fluorescence spectra at a front surface geometry.

## Results and discussion

### Synthesis of the materials

#### *Synthesis of neat silsesquioxane films*

The silane precursor was obtained by reaction of DA (1 mol) with GPTMS (2 mol), as previously described [25];

however, in order to obtain thin films (instead of the polymer as a fine powder), several modifications to the original methodology for the silsesquioxanes synthesis were introduced here. During the sol–gel poly-condensation process, the oligomers were hydrolyzed incorporating stoichiometric amounts of water and a small amount of formic acid (used as catalyst). The low content of acid employed here diminishes the poly-condensation rate and allows the bridge group to accommodate in the matrix to obtain flexible thin films.

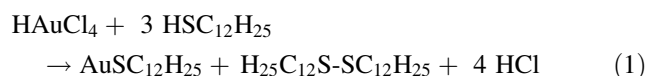
The neat silsesquioxanes films were synthesized employing stoichiometric amounts of DA and GPTMS. The reaction to obtain the precursor was carried out in 0.4 M THF solution, at  $58^\circ\text{C}$  for 48 h under nitrogen atmosphere, attaining complete conversion. The hydrolysis and condensation was performed at room temperature, employing 0.1 M solutions in THF adding an appropriate amount of water and catalyst to obtain the molar ratio  $\text{Si}/\text{HCOOH}/\text{H}_2\text{O} = 1/0.1/3$ . In all cases, 25 mL of the solutions was cast in polyacetal recipients of 5 cm diameter with an initial height of liquid close to 5 mm and covered with aluminum to enable the control of the solvent evaporation rate.

These recipients were placed in an oven at  $35^\circ\text{C}$  for 24 h. After this period, light yellow films of approximately 500  $\mu\text{m}$  thickness were formed. The films were quite flexible and were easily detached from the polyacetal mold.

The molecular structures of the reagents and a schematic representation of the synthesis are shown in Scheme 1a, b.

#### *Synthesis of silsesquioxane films containing Au(I)-DDT*

Au(I)-DDT was generated in situ in the formic acid solution of the precursor in THF, using a molar ratio of Au(I) with respect to the precursor equal to  $10^{-3}$  and a molar ratio of DDT with respect to Au(I) equal to 5:1 (DDT excess with respect to the stoichiometric value). The necessary amount of DDT was first added as a THF solution, followed by the dropwise addition of the  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  solution in THF with continuous vigorous stirring. The solution became cloudy as the generation of Au(I)-DDT took place according to the following reaction:

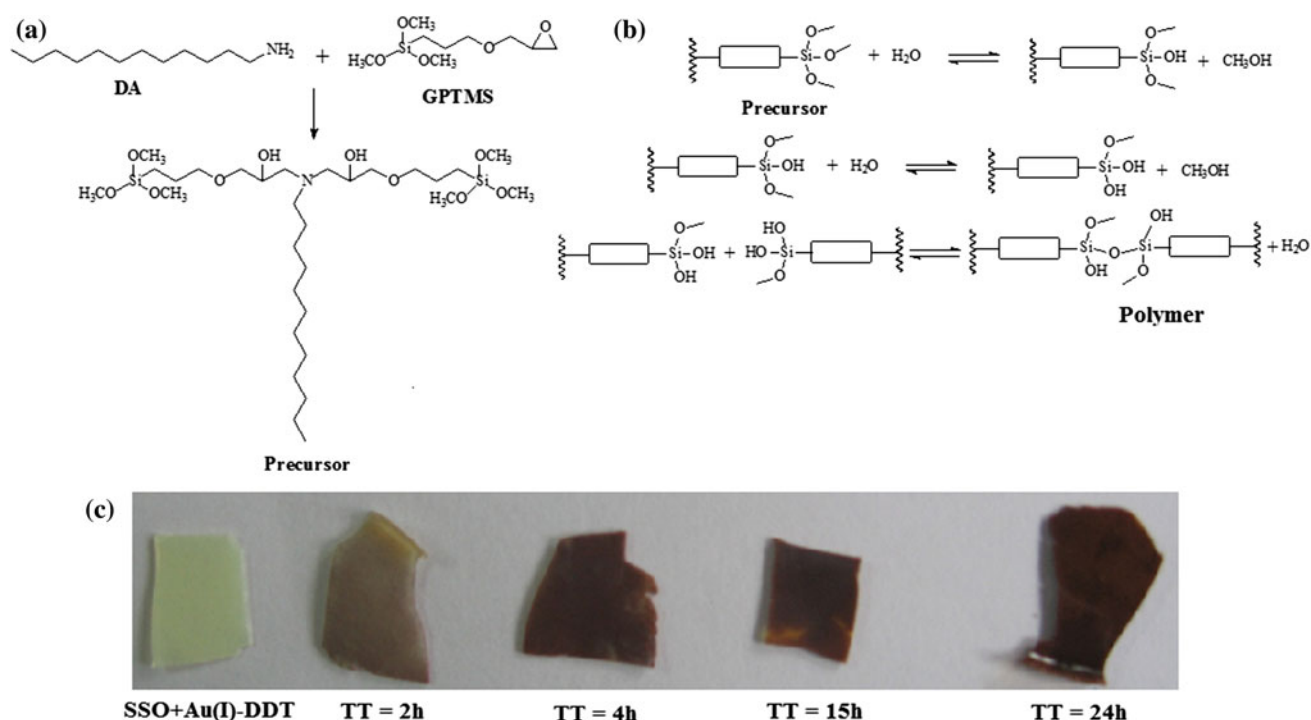


After the addition of the gold salt, the dispersion was cast in a polyacetal mold, covered with an aluminum foil and placed in an oven at  $35^\circ\text{C}$  for 24 h. Yellow films of about 500  $\mu\text{m}$  thickness were obtained and easily removed from the polyacetal mold.

#### *Synthesis of gold nanocomposites*

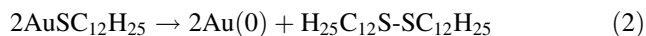
Part of the films was reserved for further analysis and small portions of them were subjected to thermal treatment (TT),





**Scheme 1** Schematic representation of the synthesis of the precursor (a), its hydrolysis and (partial) condensation to produce the corresponding silsesquioxanes (b). Photograph of SSO doped with Au(I)-DDT without and with TT (c)

by placing the samples in an oven at 150 °C for different periods of time 2, 4, 15, and 24 h. Upon heating, the generation of Au(0) takes place inside the matrix as result of Au(I)-DDT thermolysis, with the formation of disulfide as a side product [19]:



A picture of the obtained materials can be observed in Scheme 1c.

#### Characterization of the synthesized materials

##### Neat silsesquioxane films

Neat silsesquioxane films with a thickness around 500  $\mu\text{m}$  were flexible, transparent, and light yellow materials. Immersion tests in water, buffer solution with pH 7 and ethanol, for 7 days at room temperature ( $20 \pm 2$  °C) showed that the films were stable but exhibited some swelling (<4 %) in the aqueous media. The contact angle of water on the film surface was  $103 \pm 5^\circ$ , which is close to the one reported for poly(tetrafluoroethylene) [26, 27], indicating the high hydrophobicity of the silsesquioxane films.

The thermal stability of films was investigated by DSC. Cells containing the samples were weighed before and after the heating to 250 °C. A small weight loss was observed

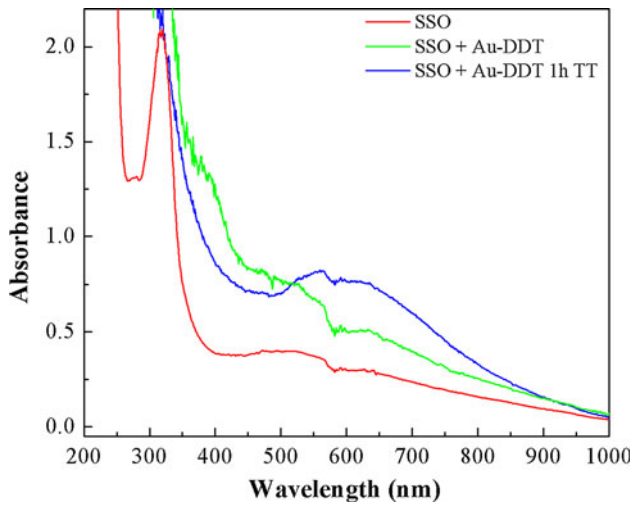
after the first scan, assigned to evaporation of volatiles. However, second and subsequent scans did not show any further mass loss giving evidence of the thermal stability of the silsesquioxane in this temperature range.

As silsesquioxanes show photoluminescence [21, 28–30], this property was analyzed in the synthesized films. Absorption spectra of the films are shown in Fig. 1. The neat silsesquioxane shows a significant absorption peak in the UV range and a very low absorption in the visible range.

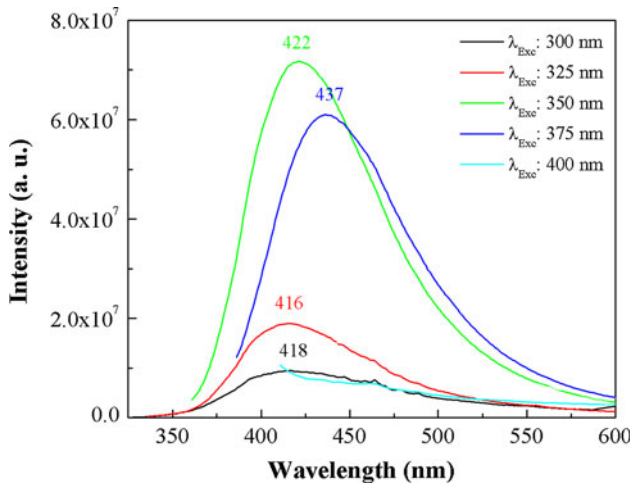
Figure 2 shows photoluminescent spectra of the neat silsesquioxane film for excitation wavelengths ranging from 300 to 400 nm. The film exhibited photoluminescence for excitation wavelengths comprised between 300 and 375 nm. An emission maximum located at 422 nm was found when exciting at 350 nm. Excitation spectra (Fig. 3) show a maximum emission at 425 nm when exciting at 352 nm. The emission and excitation maxima shifted progressively to the red as the excitation and emission wavelength was increased. The contribution of at least two different species to the photoluminescence is clearly seen from the excitation spectra. Similar results were observed before for other silsesquioxane films [28, 29].

##### Silsesquioxane films containing Au(I)-DDT

The absorption spectrum of the film containing Au(I)-DDT is shown in Fig. 1. An absorption shoulder at about 400 nm



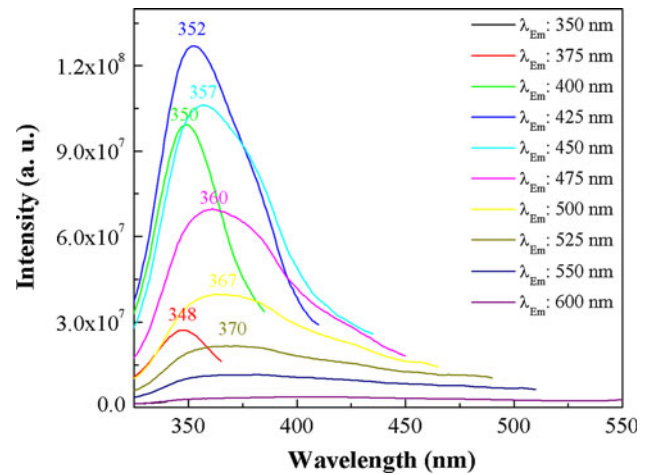
**Fig. 1** Absorption spectra of the neat silsesquioxane (SSO) film and of films containing Au(I)-DDT without thermal treatment (TT) and after 1 h at 150 °C (the steep change at about 580 nm is an artifact)



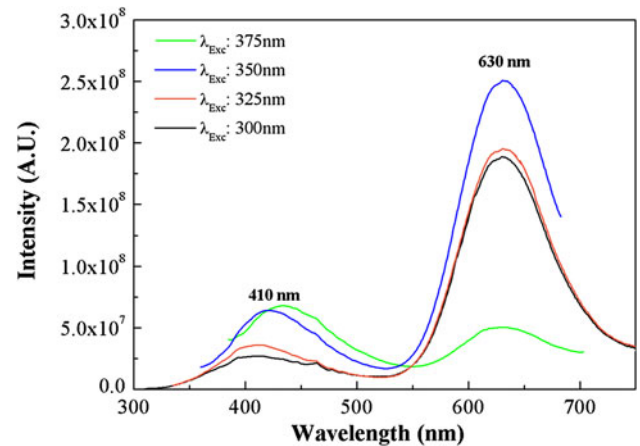
**Fig. 2** Emission spectra of the neat silsesquioxane obtained with excitation wavelengths comprised between 300 and 400 nm

is superimposed on the absorption spectrum of the neat silsesquioxane.

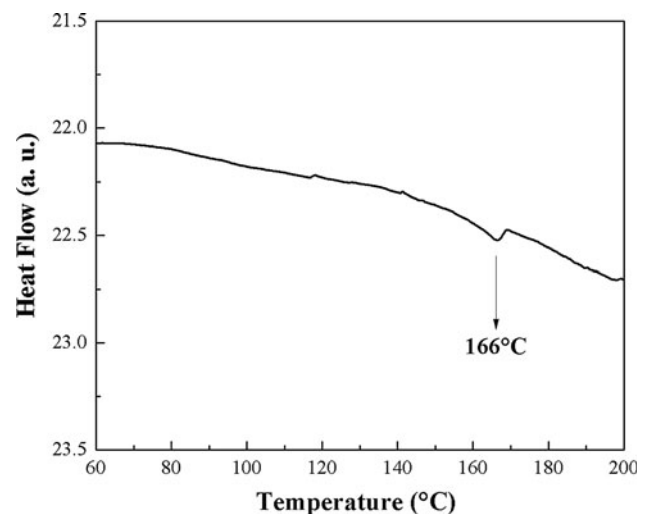
The emission spectra are shown in Fig. 4, and basically correspond to the emission of Au(I)-DDT [18]. The spectrum has two well-defined emission bands centered at about 410 and 630 nm. Bachman et al. [31] assigned the high and low energy emission bands to ligand to metal charge transfer—derived state and a triplet metal-center state, respectively. The band assigned to the high energy emission (~410 nm) of the thiolate should overlap in some extent with the emission of the neat silsesquioxane. These results demonstrate that Au(I)-DDT was efficiently formed in the silsesquioxane matrix.



**Fig. 3** Excitation spectra of neat silsesquioxane films obtained at emission wavelengths varying from 350 to 600 nm



**Fig. 4** Emission spectra of silsesquioxane films containing Au(I)-DDT



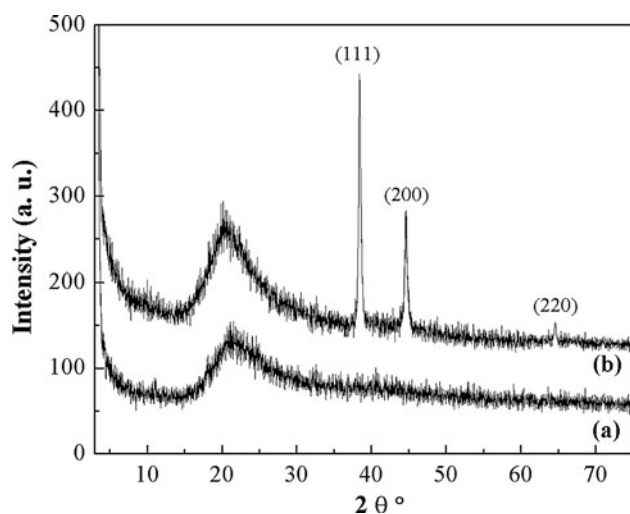
**Fig. 5** DSC thermogram of the film containing Au(I)-DDT

### Gold nanocomposites

Heating of the films containing Au(I)-DDT for different periods of time at 150 °C produced a significant change in the appearance of the films. They turned from yellow to brown and dark brown when increasing the heating period.

The absorption spectrum of a film heated for 1 h at 150 °C shows the presence of a broad band with a maximum at about 600 nm (Fig. 1), assigned to the plasmon band of relatively large metallic gold NP [20, 32]. The resulting films were no longer photoluminescent giving extra evidence of the transformation of Au(I)-DDT into gold NP [19].

The formation of Au(0)NPs by thermal decomposition of Au(I)-DDT may be also evidenced in DSC thermograms. The melting peak of Au(I)-DDT at 166 °C (Fig. 5) disappeared after the TT of the films [19].

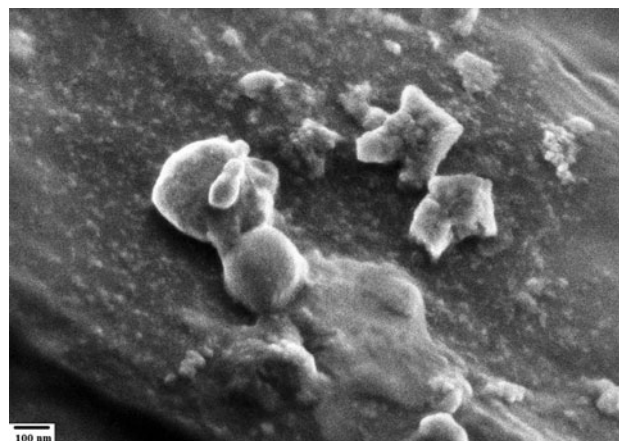


**Fig. 6** X-ray diffraction spectra of the silsesquioxane containing Au(I)-DDT, **a** as synthesized, **b** after 24 h heating at 150 °C

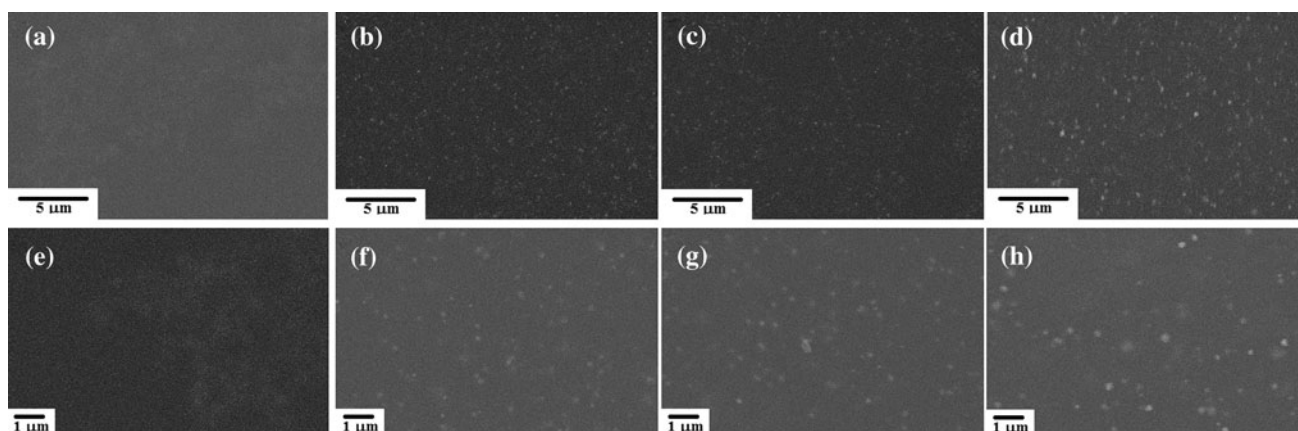
X-ray diffraction spectra (Fig. 6) also show the generation of metallic gold by the TT. After 24 h heating at 150 °C, characteristic peaks of metallic gold appear in the diffraction spectrum superimposed to the amorphous band of the neat silsesquioxane. Peaks at  $2\theta = 38.3^\circ$  and  $44.5^\circ$  correspond to the diffraction of (111) and (200) crystalline planes, respectively. A very small peak assigned to the (220) plane is also observed at  $2\theta = 64.3^\circ$  [16].

The distribution and typical sizes of the generated gold NP may be observed in SEM micrographs of the film surface (Fig. 7). Particles with sizes in the order of 100–200 nm are uniformly distributed in the whole sample. A FE-SEM micrograph (Fig. 8) shows the presence of a broad distribution of particle sizes, with some of them attaining dimensions in the order of several hundreds of nanometers.

EDAX was used to confirm that the particles were composed of metallic gold. In the black areas of the SEM image shown in Fig. 9, EDAX revealed the presence of Si,

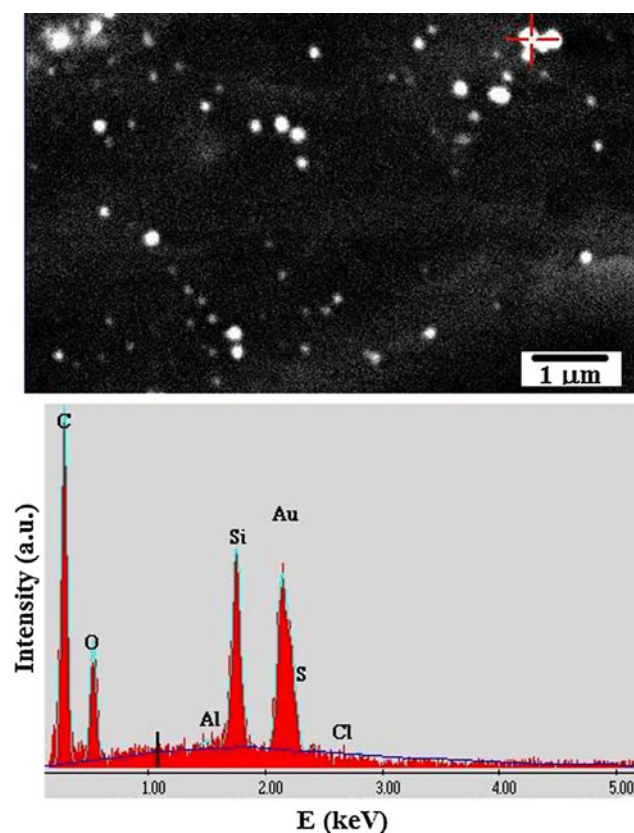


**Fig. 8** FE-SEM micrograph of the film obtained after 24 h heating at 150 °C



**Fig. 7** SEM micrographs of films at different exposition times of heating at 150 °C: 0 h (**a** and **e**), 2 h (**b** and **f**), 4 h (**c** and **g**), and 15 h (**d** and **h**). Obtained at different magnifications:  $\times 5000$  (*top*) and  $\times 10000$  (*bottom*)





**Fig. 9** SEM–EDAX analysis of the film obtained after 24 h heating at 150 °C

C, and O of the neat silsesquioxane. In the brilliant spots, the presence of metallic Au was dominant.

## Conclusions

Photoluminescence of Au(I)-DDT and its thermal reduction to metallic gold have been extensively reported in the previous literature. But incorporation of this salt to a polymeric matrix to produce photoluminescent materials or gold nanocomposites by thermal reduction is a difficult task due to the insolubility of Au(I)-DDT. In previous reports of Au(I)-DDT/polymer blends, agglomerations could not be avoided. In this study we showed that a silsesquioxane with pendant dodecyl chains can be a convenient host to produce a uniform distribution of the Au(I)-DDT salt and the gold NP generated after thermal reduction. The similarities of chemical structures of both compounds (presence of dodecyl chains) and the in situ generation of the salt in the solution of the silsesquioxane precursor facilitated the dispersion. Flexible films were generated, exhibiting characteristic photoluminescent properties before TT and a uniform dispersion of gold NP after TT.

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